

Ionic Conducting Behavior in Polyether Poly(urethane urea) based Solid Polymer Electrolyte

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Introduction

Solid polymer electrolytes (SPEs) have received considerable attention in the past decade because of their possible room-temperature conductivity up to 10^{-4} S/cm and wide applications in secondary battery systems, fuel cells, and other electrochromic displays. Early work by Armand [1] and others [2] has prompted numerous investigations into the dissolution of alkali-metal salts in polyether polymers. Polyether poly(urethane urea) (PEUU) is composed of a polyether soft segment and a diisocyanate-based hard segment, being characterized by a two-phase morphology. The phase separation is due to the fact that the hard and soft phases are immiscible and leads to the formation of a hard-segment domain, a soft-segment matrix, and an ill-defined interphase [3,4]. It is interested to understand the lithium cation environments in PEUU. Here we introduced ^7Li magic angle spinning NMR spectra with high-power proton decoupling to clarify the role for ion-polymer/ion-ion interactions and the nature of the charge carrier.

Results and Discussion

In Figure 1, the ionic conductivity data for the electrolyte samples are presented against reciprocal temperature. It is evident from Figure 1 that the temperature dependency of the conductivity data follows the Arrhenius equation. This indicates that the charge carriers are decoupled from the segmental motion of the polymer chain and transport occurs via an activated hopping mechanism. As is evident from Figure 1, the relationship between conductivity and salt concentration is a complex one. At lower temperature regions higher salt containing electrolytes have lower conductivity, whereas at higher temperature region the reverse relationship was observed. Samples containing higher amount of salt improve conductivity by increasing the number of charge carriers, but the T_g of the polymer is also simultaneously increased, which decreases the ionic mobility. Hence, at lower temperature region, the samples containing higher amount of the salt, though containing increased number of charge carriers show lower conductivities as the mobility is restricted due to higher T_g of the soft segment.

Figure 2 shows the ^7Li NMR spectra as a function of salt concentration, recorded at 220 K. At the doping level of 0.1 mmol/g LiClO_4 (Figure 2a), the intensity of site I is significantly larger than that of site II, indicating that the Li^+ cation is preferentially coordinated to site I. The intensity of site II increases with increasing salt concentration, where the intensity of site I is normalized, as shown in Figure 2c and d, and a shoulder (site III) becomes visible at lower frequency. Since site III is only observed at high salt concentration and shows a concentration dependence of its chemical shift, site III is assigned to the ion pairs or aggregates. On the basis of the conductivity mainly resulting from the lithium in the soft segment for PEUU-based electrolytes, we conclude that site II is attributable to the Li^+ cations coordinated to ether oxygen atoms in the soft segment, while site I is

associated with urethane groups in the hard segment.

References

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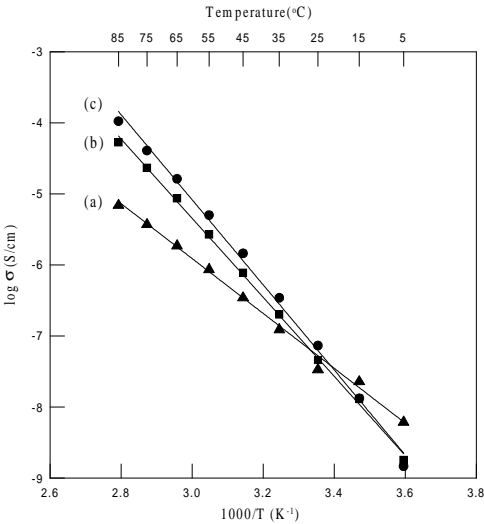


Fig. 1. Dependence of conductivity on the reciprocal of temperature for PEUU doped with various LiClO_4 concentrations: (a) 0.5, (b) 1.0, and (c) 1.5 mmol/g PEUU

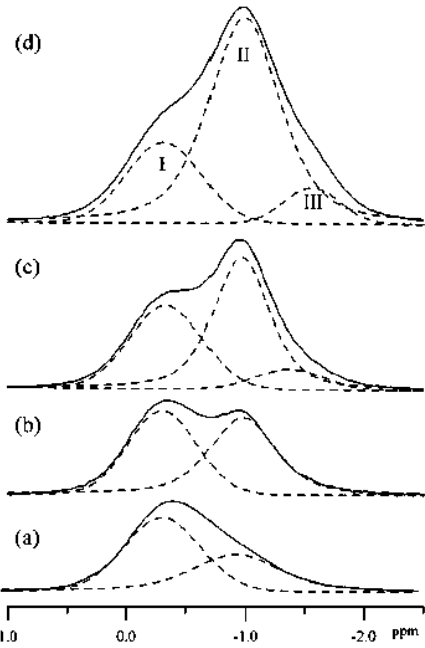


Fig. 2. Deconvolution of ^7Li proton-decoupled MAS NMR spectra at 220 K for PEUU samples doped with (a) 0.1, (b) 0.5, (c) 1.0, and (d) 1.5 mmol/g LiClO_4 .